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(54) PHOTOREACTIVE COMPOSITION, ACID-REACTIVE HIGH POLYMER COMPOSITION CONTAINING THE SAME AND ACID-REACTIVE RESIN LAYER

(57)Abstract:

PURPOSE: To obtain a photoreactive composition having improved photosensing speed through amplifying photochemical reaction by using as the components of the composition, a photo- acid-generating agent that generates acid with the effect of light and an acid-breeding agent that newly generates acid with the acid generated by the photo-acid-generating agent.

CONSTITUTION: This composition consists of a photo-acid-generating agent that generates acid with the effect of light and an acid-breeding agent that newly generates acid with the acid generated by the photo-acid-generating agent. Namely, by using a combination of the acid-breeding agent that newly generates acid with the catalytic effect of acid and the photo- acid generating agent, for example, one acid molecule is generated and, one molecule of the acid-breeding agent is decomposed by one acid molecule generated with the photo-acid- generating agent into newly formed one or more acid molecules and therefore, the one or more acid molecules are bred into two or more acid molecules by each acid-catalytic reaction and thus, these reactions are caused in a chainlike manner to increase the acid molecules in a geometrical-progressional manner. By adding the acid-breeding agent having such characteristics, the amount of acid is rapidly increased and as a result, termination of the acid-catalytic reaction due to any basic substance and disappearance of the acid by any side reaction can be prevented from occurring and thereby, the acid-catalytic reaction can be accelerated.

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CLAIMS

[Claim(s)]

[Claim 1] A photoreaction nature constituent which consists of a photo-oxide generating agent which generates an acid according to an operation of light, and an acid growth agent which newly generates an acid with an acid generated from this photo-oxide generating agent.

[Claim 2] An acid reactive polymer constituent characterized by making a photo-oxide generating agent which generates an acid according to an operation of light, and an acid growth agent which newly generates an acid according to an operation of this acid exist in a high polymer which mixed material which produces molecular structure change according to an operation of an acid, or a high polymer which combined residue which produces molecular structure change according to an operation of an acid.

[Claim 3] An acid reactivity resin layer characterized by providing the following An acid growth agent which newly generates an acid with an acid generated from said photo-oxide generating agent in a resin layer which consists of a high polymer which mixed material which produces molecular structure change according to an operation of an acid or a high polymer which combined residue which produces molecular structure change according to an operation of an acid, and a photo-oxide generating agent Two-layer structure which carried out the laminating of the different resin layer from the aforementioned resin layer which consists of a high polymer which mixed material which produces molecular structure change according to an operation of a newly generated acid, or a high polymer which combined residue which produces molecular structure change according to an operation of an acid

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the acid reactive polymer constituent and acid reactivity resin layer containing this photoreaction constituent further about the photoreaction constituent which raised sensitization speed by combining the material (it being hereafter called an acid growth agent) which newly generates an acid with the generated acid with the material (it being hereafter called a photo-oxide generating agent) which generates an acid in an operation of light.

[0002]

[Description of the Prior Art] Light energy is absorbed conventionally and it is used in the direction chemical between intramolecular or a molecule or of versatility [material / which has the photosensitive function which produces a physical change]. For example, in many fields, it is used and using as an image formation material which detects optically the chemical structural change produced by the photoreaction, or using as a surface coating processing material which performs surface treatment by the photo-curing of a monomer or a prepolymer etc. is put in practical use. However, the sensitization speed in the material which has these photosensitive functions, a sensitization wavelength field, and definition are various, and the material which has a suitable property according to the purpose is chosen.

[0003] Although silver salt sensitive material was used more widely in ancient times as a material which has a photosensitive function, the photopolymer which uses polymeric materials as a principal component reaches far and wide as extensive and the high sensitivity image formation material in which high definition is shown, and it came (refer to the volume Yamaoka Tsugio and for Gentaro Matsunaga, "photopolymer technology", and Nikkan Kogyo Shimbum (1988)) to be used in recent years. [as / in photoengraving-process technology etc.] The macromolecule system photosensitivity material is not only excellent in definition, but can set up a wide range sensitization wavelength field by selection of the photoreaction. Moreover, it has many advantages of being able to manufacture comparatively cheaply. However, sensitization speed is very low in comparing with a silver salt photosensitivity material, and also although it is called the high sensitivity macromolecule system photosensitivity material, the present condition is not amounting to 1/1000 of the sensitization speed which a silver salt material's shows.

[0004] In order to raise the sensitization speed of a macromolecule system photosensitivity material, various attempts have so far been made. It is the photopolymerization system to which having been most widely set as the object of development carries out the polymerization of many vinyl monomers continuously by making into an initiator the radical kind generated in an operation of light. However, since the oxygen in air and the radical kind which reacts easily are growth kinds, it ends, without completing sufficient chain reaction. Moreover, with advance of a radical polymerization reaction, diffusion of a monomer is quickly controlled for the network structure within the macromolecule matrix formed rapidly, and a polymerization cannot be completed. For such a cause, essential threshold value exists in the sensitization speed of a photopolymerization system.

[0005] Creation of various macromolecule system photosensitivity materials was attained by generating an acid in an operation of light and on the other hand, combining not only the cationic polymerization that makes this acid a catalyst but various acid catalyzed reactions. Although high sensitivity is expected since there is no halt effect of the reaction by oxygen unlike a radical polymerization, sensitization speed of the present condition is rather lower in cationic polymerization, than a radical polymerization system in fact for the moisture in air, or network structure formation. Moreover, let it be a principle to heat-treat, after generating an acid with light, and to carry out induction of the acid catalyzed reaction with the macromolecule system photosensitivity material incorporating an acid catalyzed reaction. For this reason, this kind that makes a photoresist a main use gestalt of macromolecule system photosensitivity material is called the chemistry amplification mold photoresist. However, the present condition is that sensitization speed is less than a radical polymerization system, and improvement in a fast sensitization speed has still been called for.

[0006] Furthermore, by using an optical radical polymerization and optical cationic polymerization, or combining the both, the resin constituent which hardens a film-like resin coat to a high degree of hardness by optical exposure is also large liquefied, and practical use is presented. Although the optical cationic polymerization system which does not receive the inhibition effect by the oxygen in air is widely set as the object of development research and development of the monomer and prepolymer suitable for the photo-oxide generating agent suitable for hardening or hardening is performed actively in recent years, improvement in a cure rate is called for for speeding up of a hardening production process. Furthermore, since hardening of the resin constituent and the thick coat which the

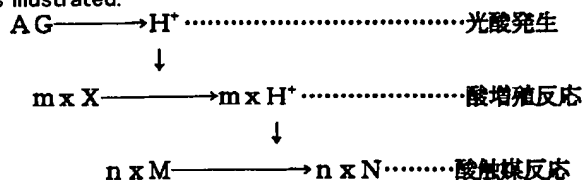
pigment which absorbs light distributed takes place only by the surface layer, the essential trouble that sufficient hardening is not brought about has resulted as it is not solved. Moreover, it thinks for the base component of the minute amount which floats in air to bring about a poisoning operation of a catalyst as a cause by which it will not become so high although the sensitization speed of the above-mentioned chemistry amplification mold photoresist uses the acid catalyzed reaction, or the acid catalyzed reaction in the inside of a macromolecule matrix triggers side reaction, and it is also considered that an acid catalyzed reaction stops for this reason.

[0007]

[Problem(s) to be Solved by the Invention] The result to which this invention person examined various the methods of solving such a situation radically, It is what completed a header and this invention for the photoreaction constituent which raised sensitization speed remarkably by combining the material which newly generates an acid with the generated acid with the material which generates an acid in an operation of light. The purpose of this invention offers the photoreaction constituent which was made to amplify photochemical reaction and raised sensitization speed remarkably.

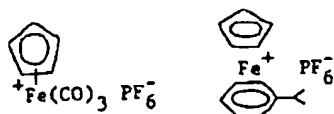
[0008]

[Means for Solving the Problem] A photo-oxide generating agent in which a summary of invention of the 1st of this application generates an acid according to an operation of light, It is the photoreaction nature constituent which consists of an acid growth agent which newly generates an acid with an acid generated from this photo-oxide generating agent. A photo-oxide generating agent which generates an acid according to an operation of light in a high polymer which mixed material from which a summary of the 2nd invention produces molecular structure change according to an operation of an acid, or a high polymer which combined residue which produces molecular structure change according to an operation of an acid, It is the acid reactive polymer constituent characterized by making an acid growth agent which newly generates an acid according to an operation of this acid exist. A high polymer which mixed material from which a summary of the 3rd invention produces molecular structure change according to an operation of an acid, Or an acid growth agent which newly generates an acid with an acid generated from said photo-oxide generating agent in a resin layer which consists of a high polymer which combined residue which produces molecular structure change according to an operation of an acid, and a photo-oxide generating agent, The aforementioned resin layer which consists of a high polymer which mixed material which produces molecular structure change according to an operation of a newly generated acid, or a high polymer which combined residue which produces molecular structure change according to an operation of an acid is an acid reactivity resin layer which has two-layer structure which carried out the laminating of the different resin layer. Namely, by combining with a photo-oxide generating agent an acid growth agent which newly generates an acid according to an operation of an acid in this invention Since one acid is generated, and this acid disassembles an acid growth agent molecule and newly generates one or more acids from a photo-oxide generating agent according to an operation of light One or more acid-content children will increase at one reaction, it will become a total of two or more acid-content children, this reaction will arise continuously, and generating of an acid will increase in multiplying like rats. That is, by addition, an acid can also prevent a halt of an acid catalyzed reaction by increase, consequently alkali rapidly, and disappearance of an acid by side reaction can also prevent an acid growth agent with such a property, and an acid catalyzed reaction can be accelerated sharply. It is as follows when a principle of an above-mentioned reaction principle is illustrated.



AG Photo-oxide generating agent; X Acid growth agent; M Acidolysis product; N The acidolysis products m and n are molecularity. An organic compound which increases such an acid was used, and a growth reaction which generates an acid in multiplying like rats was not known at all as an organic chemistry reaction until now, although it was similar to a nuclear fission reaction or explosive reaction. Although it is thermally stable as much as possible, an acid decomposes and an acid growth agent generates strong acid itself, it is the compound replaced by residue of a comparatively strong acid, and triggers an elimination reaction comparatively easily and generates an acid. Therefore, although it is stable under un-existing [of an acid] if this elimination reaction can be sharply activated by acid catalyzed reaction, under existence of an acid, it becomes possible to make thermal reaction generate an acid easily. By combining an acid growth agent with such a property with a photo-oxide generating agent, a photosensitive material whose sensitization speed improved by leaps and bounds became possible.

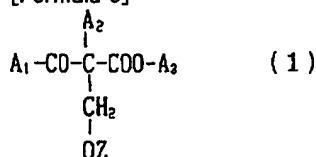
[0009] This invention is explained to details. As a photo-oxide generating agent which generates an acid according to an operation of light in this invention, a compound used for a chemistry amplification mold photoresist or optical cationic polymerization is used (a volume on organic electronics material study group, "imaging business refer to organic material", the *** exudation version (1993), and 187 - 192 pages). An example of a suitable compound for this invention is given to below. Moreover, in order to expand a sensitization wavelength field of these photo-oxide generating agents, a photosensitizer can also be made to live together suitably. With the acid active substance, an acid generated by photolysis of such material acts on an acid growth agent, and promotes generating of an acid. The following photo-oxide generating agents can be used. PF6- of aromatic series onium compounds, such as diazonium,



[0017] The acid growth agent used by this invention is the compound replaced by the residue of a comparatively strong acid, and is a compound which triggers an elimination reaction comparatively easily and generates an acid. Therefore, this elimination reaction can be sharply activated by the acid catalyzed reaction, and although it is stable under un-existing [of an acid], under existence of an acid, it becomes possible to make thermal reaction generate an acid easily. By combining an acid growth agent with such a property with a photo-oxide generating agent, the photoreaction nature constituent whose sensitization speed improved by leaps and bounds became possible. An acid catalyzed reaction decomposes and an acid (it is ZOH at the following general formulas) is generated again. One or more acids are increasing in number at one reaction, and a reaction progresses accelerative with advance of a reaction. In order for the generated acid itself to carry out induction of the autolysis, reinforcement of the acid generated here is set to an acid dissociation constant and electric dissociation exponent, and is three or less, and it is desirable that it is two especially or less. An autolysis cannot be caused if it is an acid weaker than this. As such an acid, dichloroacetic acid, a trichloroacetic acid, methansulfonic acid, ethane sulfonic acid, benzenesulfonic acid, p-toluenesulfonic acid, a naphthalene sulfonic acid, triphenyl phosphonic acid, etc. can be raised. Specifically, the following compounds can be illustrated. The organic-acid ester compound expressed [1st] with a general formula (1) can be mentioned.

[0018]

[Formula 5]

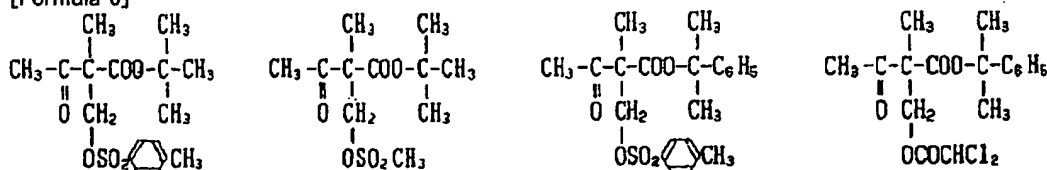


[0019] (A1 shows the alkyl group or aryl group from C1 to C6 among a formula, A2 shows the alkyl group from C1 to C6, and A3 is screw (p-alkoxy phenyl) methyl) A radical, a 2-alkyl-2-propyl group, a 2-aryl-2-propyl group, a cyclohexyl radical, or a tetrahydropyranyl group is shown, and Z shows the residue of the acid shown by ZOH whose acid dissociation constant (electric dissociation exponent) is three or less.

If an acid acts on this compound, an ester group decomposes and it becomes a carboxylic acid, and after this raises a decarboxylic acid further, an acid (ZOH) will **** easily. Specifically, an example is shown below.

[0020]

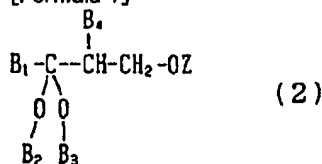
[Formula 6]



[0021] Organic-acid ester with the acetal or ketal radical expressed [2nd] with a general formula (2) can be mentioned.

[0022]

[Formula 7]

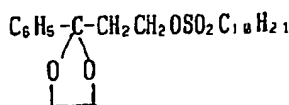
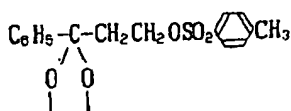


[0023] (Z has the same semantics as the above among a formula, B1 is a hydrogen atom, an alkyl group, or an aryl group, B-2 and B3 form ethylene or a propylene radical in methyl, an ethyl group, or both, and B4 shows a hydrogen atom or a methyl group)

An acetal or ketal decomposes in an operation of an acid, this compound serves as beta-aldehyde or a ketone, and ZOH is easily desorbed from it after this. A concrete example is shown below.

[0024]

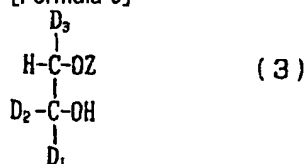
[Formula 8]



[0025] The organic-acid ester expressed [3rd] with a general formula (3) can be mentioned.

[0026]

[Formula 9]

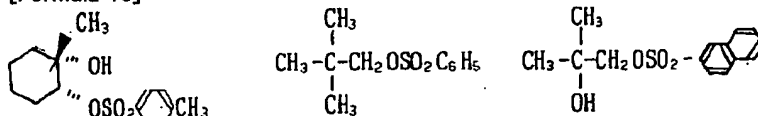


[0027] (Z has the same semantics as the above among a formula, D1 and D2 show a hydrogen atom, the alkyl groups from C1 to C6, or an aryl group, and D2 and D3 show the alkylene or substitute alkylene residue which forms alicycle-like structure on the alkyl group or both sides from C1 to C6)

After a hydroxyl group ****s, and this compound forms carbocation and carries out hydrogen migration according to an acid catalyst, it is presumed to be what ZOH generates. A concrete example is shown below.

[0028]

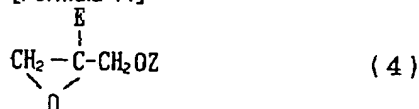
[Formula 10]



[0029] The organic-acid ester which has the epoxy ring expressed [4th] with a general formula (4) can be mentioned.

[0030]

[Formula 11]

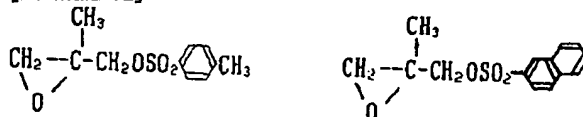


[0031] (Z has the same semantics as the above among a formula, and E shows the alkyl groups or phenyl groups from C1 to C6)

If an acid acts on this compound, a cation will be formed in beta-carbon with generation of the ring breakage of an epoxy ring, and what an organic acid generates as a result of hydrogen migration will be presumed. A concrete example is shown below.

[0032]

[Formula 12]

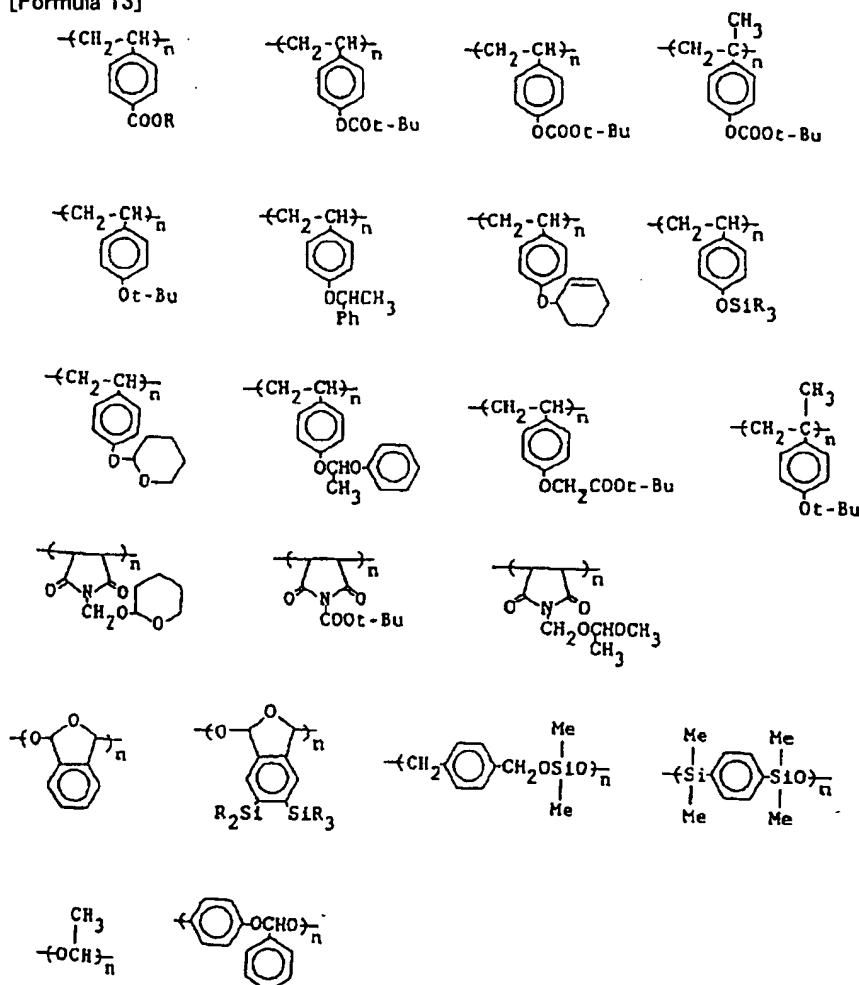


[0033] These compounds exist in stability at a room temperature, unless an acid acts. Although the acid strength more than fixed is needed in order to cause acid-catalyst disassembly of these compounds, it is desirable that it is about two or less in an acid dissociation constant pka. If it is the acid dissociation constant beyond this, i.e., a weaker acid than this, the reaction of an acid growth agent cannot be triggered.

[0034] Next, the high polymer which mixed the material (acid reactivity molecule) which produces molecular structure change according to an operation of the acid in which the above-mentioned photoreaction constituent is made to exist, or the high polymer which combined the residue which produces molecular structure change according to an operation of an acid is explained. In addition, the material or residue which produces molecular structure change is only called an acid reactivity molecule or acid reactivity residue. The example of a high polymer which mixes, or joins together and becomes about the acid reactivity molecule used suitable for this invention is shown (the volume on organic electronics material study group, "imaging business refer to organic material", the

**** exudation version (1993), and 199 - 201 pages). many use the reaction of the deprotection radical in synthetic organic chemistry — **** (T. refer to W.Greene, Protective Groups in Organic Synthesis, and John Wiley & Sons (1981)) — a concrete example is shown below. The high polymer which has acid reactivity residue in a side chain or a principal chain can be mentioned to the 1st. As acid reactivity residue, the phenol nature or N-methylol nature hydroxyl group protected by the 2nd class, the 3rd class ester, the tetrahydropyranyl ester, the 3rd class ester of carbonic acid, trialkylsilyl group, and tetrahydropyranyl group of a carboxylic acid is used suitably. Since a deprotection reaction occurs and a polar high carboxylic acid and a polar high phenol generate these according to an operation of an acid, the exposure section is solubilized in a polar solvent or an alkali aqueous solution. High sensitivity sensitive material is one of things using such a property. As the example of a concrete compound, [0035]

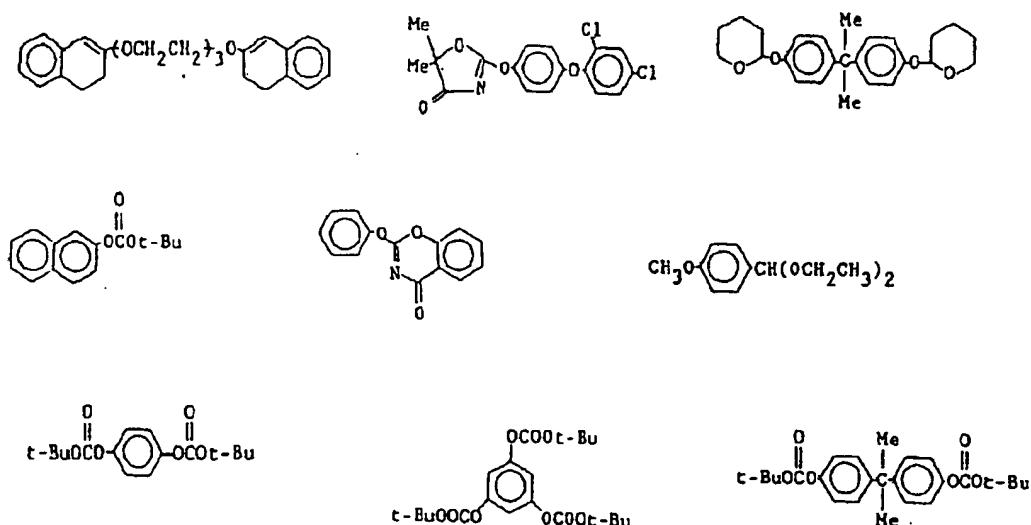
[Formula 13]



[0036] The high molecular compound containing an acid reactivity low molecular weight compound is in the 2nd. Here, an acid reactivity low molecular weight compound has the effect of reducing the solubility of a resin compound, and is called a dissolution inhibitor. As a dissolution inhibitor, phenols, a pinacol derivative, etc. which were protected by an acetal compound, a ketal compound, the 3rd class ester of a carboxylic acid, tetrahydropyranyl ester, the 3rd class ester of carbonic acid, the trialkylsilyl group, or the tetrahydropyranyl group can be mentioned. As a resin compound containing these dissolution inhibitors, novolak resin, Pori (p-hydroxystyrene), a methacrylic-acid copolymer, N-methylol maleimide copolymer, etc. can be raised. Although a low molecular weight compound has the effect which checks the solubility over the alkali aqueous solution of these resin, by decomposing in an operation of an acid, this dissolution depressor effect is lost and a macromolecule serves as alkali solubilization. A concrete dissolution inhibitor is illustrated below.

[0037]

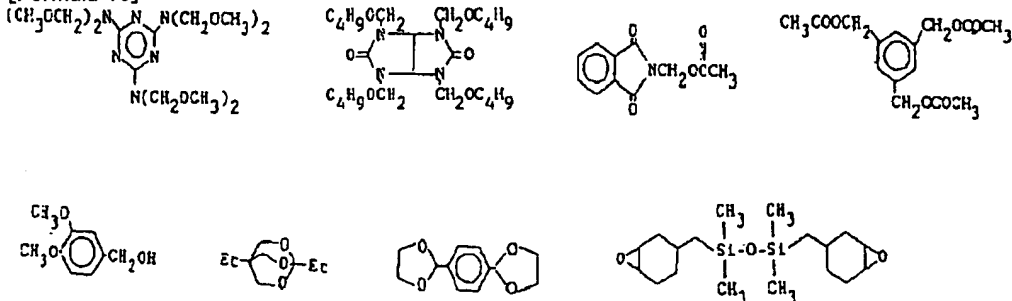
[Formula 14]



[0038] The condensation reaction by the acid catalyzed reaction is used [3rd] for the crosslinking reaction of a macromolecule. As residue which forms a cation and causes a condensation reaction by the acid catalyst, a benzyl alcohol derivative, a melamine derivative, N-methylol imide derivative, an acetal derivative, a vinyl ether derivative, etc. can be raised. Moreover, as generated KAOCHIN and residue which reacts, a phenol, alcohol, etc. can be mentioned and polymer ** of the macromolecule which has such residue, for example, the polymer of p-hydroxystyrene, novolak resin, and hydroxyethyl methacrylate is used suitably. The compound which causes a condensation reaction is illustrated below.

[0039]

[Formula 15]



[0040] Moreover, since the macromolecule having this condensation nature residue and phenyl residue causes bridge formation by the acid catalyst by itself, it is convenient for this invention. A macromolecule with the residue which carries out [4th] a polymerization according to an acid catalyst is used. As cationic polymerization nature residue, an epoxy group, oxetane residue, a vinyl ether radical, an isopropenyl phenyl group, annular orthochromatic ester, etc. can be raised. The constituent set to the 5th from a cationic polymerization nature monomer or a prepolymer is also used. As a cation nature monomeric unit, an epoxy group, an oxetane radical, a vinyl ether radical, and annular orthochromatic ester are used. It is desirable to mix with a vinyl system polymer and to use these monomers or prepolymers as the filmy material of self-support nature.

[0041] Subsequently, the adjustment method of the photopolymer constituent of this invention is described below. To the high molecular compound which is acid reactivity, the resin or itself containing low-molecular material with an acid reactivity unit adds 0.5 - 20% of the weight of a photo-oxide generating agent, and 0.1 - 20% of the weight of an acid growth agent to it. Since many of above-mentioned photo-oxide generating agents generate a radical kind with an acid, it can also mix with a radical polymerization nature monomer or a prepolymer with the acid active substance. Furthermore, a pigment, a color, etc. may be added suitably.

[0042] In order to distribute to homogeneity, it is desirable to dissolve each liquefied. It exposes, after making these constituents into the shape of a film, and the acid as a latent image is generated. Subsequently, while performing heating (postbake) processing and urging a chain of decomposition of an acid growth agent, an acid catalyzed reaction causes a structural change of the acid active substance. although the conditions of heat-treatment are changed according to the class of residue [activity / acid / exposure energy and / to be used], the class of macromolecule, etc. — heating temperature — the range of 60 to 150 degrees — it is the range of 80 to 130 degrees more preferably. Heating time is 5 minutes from 30 seconds more preferably from 10 seconds for 10 minutes. If heating time is short more than this, an acid catalyzed reaction will not fully be triggered, in the time amount exceeding this range, an acid growth agent may trigger side reaction, and productivity is missing. The resin or itself containing the acid active substance uses change of the physical properties before and behind the exposure accompanying a structural change of the resin which is acid reactivity, and heat-treatment, for example, solubility, a

degree of hardness, thickness, viscosity, gassing, etc. Furthermore, it can divide into the resin layer which contains a photo-oxide generating agent in this invention, and the resin layer containing an acid growth agent, and can consider as two-layer structure. Next, this invention is explained still more concretely with an example.

[0043]

[Example] The synthetic example of the typical acid growth agent which can be first used by this invention is shown as an example of reference.

It was made to react to the 2-methyl-3-keto butanoic acid tert butyl ester which example of reference 1 acetoacetic-acid tert-butyl ester was made to react with a methyl iodide, and obtained it under existence of the sodium hydride in THF with formalin in ethanol under existence of a potassium hydroxide. The 2-hydroxymethyl-2-methyl-3-keto butanoic acid tert butyl ester generated at 40% of yield was made to react with p-tosyl chloride under existence of triethylamine in dichloromethane, and 2-methyl-2-(p-toluenesulfonyloxy)-3-keto butanoic acid tert butyl ester was obtained as oily matter. The product was refined by silica gel column chromatography -

m. p.52-53-degree-C1 H-NMR (CDCl3)

delta (ppm):1.38(s,3H,-COC(CH3)CO-),1.40(s,9H,-C(CH3)3),2.15(s,3H,CH3CO-),2.47(s,3H,Ar-CH3),4.28

(ABq,J=10Hz,2H,-CH2-OSO2-),7.38(d,J=7.7Hz,2H,Ar-H),7.77(d,J=7.7Hz,2H,Ar-H)

IR(cm⁻¹): 1738 (>C=O of ester) 3000, 1719 (>C=O)

Elemental-analysis C17H24O6Scalc. C:57.29% H:6.79% S:9.00%found C:57.18% H:6.90% S:8.84% [0044] Like example of reference 2 example 1, methansulfonic acid chloride was used instead of p-tosyl chloride, and 2-methyl-2-methane sulfonyloxy-3-keto butanoic acid tert butyl ester was obtained as oily matter.

1H-NMR(CDCl3)

delta (ppm):1.50 (s, 12H, -C3 (CH3)), -COC(CH3) CO-, 2.22 (s, and 3H and CH3CO-), 3.05 (s, 3H, -OSO2CH3), 4.50 (s, and 2H and -CH2-OSO2-)

13C-NMR(CDCl3)

delta (ppm):17.2 (CH3), and 27.2 (CH3), 27.5 (CH3), 36.9 (CH3), 59.9 (>C - <), 71.1 (>C - <), 83.1 (CH2), 168.3 (C=O) and 202.7 (C=O)

IR(cm⁻¹): 1738 (>C=O of ester) 2981, 1714 (>C=O)

Elemental-analysis C11H20O4Scalc. C:47.13% H:7.19% S:11.44%found C:47.33% H:7.45% It was made to react with 2-phenyl-2-propanol, having used sodium acetate as the catalyst, and example of S:10.3% reference 3 diketene was made into acetoacetic-acid 2-phenyl-2-propyl ester. The hydroxymethyl derivative obtained by performing methylation and methylol-ization like an example 1 in this was made to react with p-tosyl chloride, and 2-methyl-2-(p-toluenesulfonyloxy)-3-keto butanoic acid 2-phenyl-2-propyl ester was obtained as oily matter.

1H-NMR(CDCl3)

delta (ppm):1.39(s,3H,-COC(CH3)CO-),1.75(s,3H,-O-C(CH3)2-),1.79(s,3H,-O-C(CH3)2-),2.12(s,3H,CH3CO-),2.44 (s,3H,Ar-CH3),4.30(ABq,J=14Hz,2H,-CH2-OSO2-),7.30(s,5H,Ar-H),7.35(d,J=8.7Hz,2H,Ar-H),7.74(d,J=8.7Hz,2H,Ar-H)

IR(cm⁻¹): 1738 (>C=O of ester) 2983, 1716 (>C=O)

Elemental-analysis C22H26O6Scalc. C:63.14% H:6.26% S:7.66%found C:62.98% H:6.48% S:7.76% [0045] The methylol-ized acetoacetic-acid 2-phenyl-2-propyl ester which was obtained in the example of reference 4 example 3 was made to react with methane sulfonyl chloride, and 2-methyl-2-methane sulfonyloxy-3-keto butanoic acid 2-phenyl-2-propyl ester was obtained as oily matter.

1H-NMR(CDCl3)

delta (ppm):1.49(s,3H,-COC(CH3)CO-),1.75(s,3H,-O-C(CH3)2-),1.80(s,3H,-O-C(CH3)2-),2.20(s,3H,CH3CO-),2.90 (s,3H,-SO2CH3),4.48(dd,J=13Hz,2H,-CH2-O-),7.30(s,5H,Ar-H)

IR: 1738 (>C=O of ester) 2985, 1714 (>C=O)

The example of reference 51-methyl hexene was oxidized under existence of osmium oxide, and the cis-1-methyl 1 and 2-dihydroxy hexane were obtained. This was made to react under existence of p-tosyl chloride and triethylamine, and the cis-1-methyl-1-hydroxy-2-(p-toluenesulfonyloxy) hexane was obtained at 82% of yield.

Colorless prism ** m.p.65-66 degree-CIR 3460, 2935, 1598, 1348, 1176cm⁻¹, 1 H-NMR delta= 1.1 (s, and 3H and -CCH3 (OH)-) (60MHz, CDCl3), (KBr) 1.9 (s, 1H, OH) 1.1-2.0 (m, 8H, -(CH2) 4-), 2.5 (s, 3H, Ar-CH3), 4.3 (ABq, 1H, and -CH(OTs)-, J = 5 or 9Hz), 7.4 (d, 2H, Ar-H, J= 8Hz), 7.8 (d, 2H, Ar-H, J= 8Hz)

[0046] The example of reference 62-methyl-3-hydroxy propene was oxidized by the tert-butyl hydroperoxide under existence of triphenyl phosphine, and the 1 and 2-epoxy-2-methyl-3-hydroxy propane was obtained. This was made to react with p-tosyl chloride under existence of triethylamine, and the 1 and 2-epoxy-2-methyl-3-(p-toluenesulfonyloxy) propane was obtained.

The colorless oily matter (NaCl) 1600 and IR 1364, 1192 or 1178cm⁻¹ 1 H-NMR (60MHz, CDCl3) delta= 1.3 (s, 3H, CH3), 2.5 (s, 3H, Ar-CH3), 2.9 (s, and 2H and -CH2O-), 7.4 (d, 2H, Ar-H, J= 8Hz), 7.8 (d, 2H, Ar-H, J= 8Hz)

After ketal-izing example of reference 7 benzoylacetic-acid ethyl ester by ethylene KURIKO-RU, it returned with 1,3-dioxolane and considered as the 3-phenyl-2 and 3-ethyl-1,3-dioxolane compound. 1, p-tosyl chloride was made to react to this under existence of triethylamine, and the crystalline 1-(p-toluenesulfonyloxy)-3-phenyl-3 and 3-ethylene dioxo propane were obtained with about 70% of yield.

Colorless oily matter m.p.48-50 degree-CIR 2892, 1597, 1354, 1178cm⁻¹, 1 H-NMR delta= 2.27 (t, 2H, -CH2CH2OTs, J= 8Hz) (90MHz, CDCl3), (KBr) 2.44 (s, 3H, Ar-CH3) and 3.6- 4.1 (m, 4H, and -OCH2CH2O-), 4.15 (t, 2H, -CH2CH2OTs, J= 8Hz), and 7.2- 7.5 (m, 7H, Ar-H) and 7.76 (d, 2H, Ar-H, J= 8Hz)

[0047] The 4-% of the weight cyclohexane solution of example 1 Pori (p-(tert-butoxycarbonyloxy) styrene) was prepared, and the diphenyl (p-phenylthiophenyl) sulfonium hexafluoroantimonate which is 5% of the weight (it is two-

mol % to a monomeric unit) of a photo-oxide generating agent was dissolved to this polymer. Addition of the 2-methyl-2-(p-toluenesulfonyloxy)-3-keto butanoic acid tert butyl ester which is the acid growth agent obtained in the example 1 of reference in this solution was carried out to this polymer 10% of the weight (it is six-mol % to a monomeric unit). It considered as the thin film which carries out spin spreading of this solution on a silicon wafer, and has 0.5-micrometer thickness, and prebake processing was performed for this for 1 minute at 100 degrees C. For the comparison, the poly membrane which does not contain an acid growth agent was prepared similarly. These poly membranes were drawn for 7 minutes, and after changing time amount and carrying out UV irradiation of each, postbake processing was performed at 100 degrees C. Since the acid decomposed and thickness reduced this macromolecule, thickness change was measured and sensitization speed was evaluated. To the acidolysis of a macromolecule being completed by exposure for 17 seconds, when an acid amplification agent is added, in the acid growth agent additive-free case, in order for the reduction in thickness to be about 25% and to dissolve completely in the exposure for 17 seconds, the exposure for 50 seconds was required by the postbake for 2 minutes. Moreover, when an acid growth agent was added, reduction of the thickness in postbake has taken place rapidly, and the amplification effect was accepted clearly. Image formation was checked by carrying out postbake processing behind the bottom of exposure through a mask.

[0048] Instead of the diphenyl (p-phenylthiophenyl) sulfonium hexafluoroantimonate used as a photo-oxide generating agent in example 2 example 1, 6% of the weight of 2 and a 3-diphenyl-3-keto-2-hydroxy-1-(p-toluenesulfonyloxy) propane were added as a photo-oxide generating agent, and the addition effect of the 2-methyl-2-(p-toluenesulfonyloxy)-3-keto butanoic acid tert butyl ester obtained in the example 1 of reference was investigated. After carrying out spin spreading of the thin film on a silicon wafer like an example 1, postbake was performed at 100 degrees C for 3 minutes after carrying out ultraviolet-rays exposure. In the acid growth agent additive-free case, although reduction of the thickness containing an acid growth agent was rapidly completed by the exposure for 60 seconds, by the same exposure time, thickness decreased only about 15%, but in order to complete thickness reduction, it required the exposure time for 180 seconds.

3.4% of the weight of triphenylsulfonium triflate and the 2-methyl-2-(p-toluenesulfonyloxy)-3-keto butanoic acid tert butyl ester which is 1% of the weight of an acid growth agent were added to the cyclohexane solution of polymer used in the example 3 example 1 to polymer, and the thin film was prepared. After exposing ultraviolet rays, when postbake was performed at 100 degrees C for 3 minutes, the reduction in thickness was completed by the exposure for 55 seconds. In order in an additive-free case to remain in reduction of about 15% of thickness and to complete an acid growth agent by the same exposure time, the exposure time for 150 seconds was required.

[0049] 10% of the weight of diphenyl (p-phenylthiophenyl) sulfonium hexafluoroantimonate and the cis-1-methyl-1-hydroxy-2-(p-toluenesulfonyloxy) hexane obtained in the example 5 of reference were added to the cyclohexane solution of polymer used in the example 4 example 1 5% of the weight to polymer, and on the silicon wafer, spin spreading was carried out and it considered as the 0.5-micrometer thin film. After performing postbake for 2 minutes at 100 degrees C after exposing ultraviolet rays, negatives were developed by ethanol, and the residual membrane was measured. Although all the films dissolved by the exposure time for 10 seconds when an acid growth agent was added, the exposure time for 70 seconds or more was required of additive-free.

The 1 and 2-epoxy-2-methyl-3-hydroxy propane compounded in the example 6 of reference instead of the cis-1-methyl-1-hydroxy-2-(p-toluenesulfonyloxy) hexane used in example 5 example 4 was added. When UV irradiation, postbake processing, and ethanol development were performed similarly, the exposure time required in order to dissolve all films by adding an acid growth agent was able to be shortened to the quadrant.

[0050] 10% of the weight of diphenyl (p-phenylthiophenyl) sulfonium hexafluoroantimonate and the cis-1-methyl-1-hydroxy-2-(p-toluenesulfonyloxy) hexane obtained in the example 5 of reference were added to 2:1 copolymers ($M_w=4.01 \times 10^4$, $M_w/M_n=1.74$) of example 6 methyl methacrylate and methacrylic-acid 2-phenyl-2-propyl ester 5% of the weight, and on the silicon wafer, spin spreading was carried out and it considered as the 0.23-micrometer thin film. After irradiating ultraviolet rays at this, postbake processing was performed for 2 minutes at 100 degrees C, negatives were developed by ethanol, and the remaining rate of membrane was measured. By adding an acid growth agent, the exposure time required for becoming residual membrane zero was able to be shortened to the quadrant. Same exposure, postbake, and ethanol development were performed using the 1-(p-toluenesulfonyloxy)-3-phenyl -3 and 3-ethylene dioxy propane which were compounded in the example 7 of reference instead of the cis-1-methyl-1-hydroxy-2-(p-toluenesulfonyloxy) hexane used in example 7 example 6. By adding this acid growth agent, the exposure time for solubilizing all films was able to be shortened to about 1/3.

[0051] In the cyclohexanone solution of polymer used in the example 8 example 1, the diphenyl (p-phenylthiophenyl) sulfonium hexafluoroantimonate which is a photo-oxide generating agent, and the 1-(p-toluenesulfonyloxy)-3-phenyl -3 and 3-ethylene dioxy propane were added 10% of the weight to polymer, respectively, and on the silicon wafer of three sheets, spin spreading was carried out, respectively and it considered as the 0.25-micrometer thin film. After irradiating ultraviolet rays through the fenestera rotunda with a diameter of 3mm at these thin films, it heat-treated at 105 degrees C, 115 degrees C, and 125 degrees C. After the discoloration accompanying reduction in thickness appeared immediately as a round shape which is 3mm, the round shape increased with time amount. Postbake time amount until a diameter is set to 12mm was 30 seconds by 125 degrees C for 45 seconds at 115 degrees C in 105 degrees C for 7 minutes. This is because the acid generated with light is spread with heating within a poly membrane and acid generating by decomposition of an acid growth agent is caused one after another in connection with it. When an acid growth agent was not added, such reduction did not take place.

[0052] % of the 15-mol 1-(p-toluenesulfonyloxy)-3-phenyl -3 as two-mol % 2, and the 3-diphenyl-3-keto-2-

hydroxy-1-(p-TORUHEN sulfonyloxy) propane and the acid growth agent as a photo-oxide generating agent and 3-ethylene dioxy propane were added to the solution of 2-methoxy ethyl acetate of an example 9p-trimethylsilyloxy styrene homopolymer (5.35×10^4 , $M_w/M_n=1.69$). After carrying out spin spreading of this solution by 1000rpm on the silicon wafer and carrying out prebake for 30 seconds at 100 degrees C, time amount was changed, ultraviolet rays were irradiated and postbake was given for 30 seconds at 100 degrees C. When it was immersed for 10 seconds into ethanol and negatives were developed, the exposure time which a poly membrane solubilizes completely was shortened to about 1/3 compared with acid growth agent additive-free.

After adding 3% of the weight of diphenyl (p-phenylthiophenyl) sulfonium hexafluoroantimonate, and 3% of the weight of 2-methyl-2-(p-toluenesulfonyloxy)-3-keto butanoic acid tert butyl ester to the cyclohexane solution of 1:1 copolymers ($M_w=5.15 \times 10^4$, $M_w/M_n=2.04$) of example 10 methyl methacrylate and glycidyl methacrylate to this polymer, spin spreading was carried out on the anodized aluminum board. To this, time amount was changed, ultraviolet rays were exposed, and after carrying out postbake at 100 degrees C for 3 minutes, the board was washed with toluene. When compared with the case where an acid growth agent is not added, the exposure time which insolubilization of a copolymer takes was shortened to 1/5.

[0053] Addition of the 2-methyl-2-(p-toluenesulfonyloxy)-3-keto butanoic acid tert butyl ester which is the acid growth agent obtained in the example 1 of reference in the cyclohexane solution of polymer used in the example 11 example 1 was carried out to this polymer 10% of the weight (it is six-mol % to a monomeric unit). It considered as the thin film which carries out spin spreading of this solution on a silicon wafer, and has 0.27-micrometer thickness, and prebake processing was performed for this for 1 minute at 100 degrees C. For the comparison, the poly membrane which does not contain an acid growth agent was prepared similarly. 3.5% of the weight of triphenylsulfonium TORIFURA-TO was dissolved in the 0.07-% of the weight isopropyl alcohol solution of novolak resin to resin, and spin spreading was carried out on the poly membrane which prepared this previously. Prebaking for 1 minute at 100 degrees C, the film which consists of two-layer [of the film containing a photo-oxide generating agent and the film containing an acid growth agent] became the thickness of 0.62 micrometers as a whole. After exposing ultraviolet rays on this two-layer film, postbake processing was performed at 100 degrees C, and negatives were developed in 40-degree C ethanol for 1 minute. When asked for the relation between the exposure time and a remaining rate of membrane, having high-sensitivity-ized the two-layer film which added the acid growth agent 20 times compared with an additive-free two-layer film was admitted.

[0054] In example 12 example 11, when the completely same exposure as an example 10 was performed about the film of the two-layer structure which added triphenylsulfonium hexafluoroantimonate instead of triphenylsulfonium TORIFURA-TO as a photo-oxide generating agent, 18 times as many high sensitivity-ization as this was accepted by addition of an acid growth agent.

The sensitivity of the film of the two-layer structure which added the triphenylsulfonium hexafluoroantimonate prepared in the example 13 example 11, and the film which added triphenylsulfonium hexafluoroantimonate to the polymer of the example 1 which is a well-known chemistry amplification mold photoresist was measured. Consequently, the film of the two-layer structured type which separates and contains an acid growth agent showed 25 times as many high sensitivity as this to the chemistry amplification resist.

[0055]

[Effect of the Invention]

- (1) Since sensitization speed improves sharply, it can use for a high sensitivity image formation material.
- (2) Since the bridge formation effectiveness of photo-curing resin improves sharply by combining an optical exposure and heat-treatment, it can use to an ultraviolet curing mold coating, ink, a surface coating agent, etc. effectively. In the paint film which consists of a photo-curing agent which carried out pigment content powder, although it does not happen at all in that hardening is inadequate or the interior since light absorption happens only by the surface layer, according to this invention, hardening can be made perfect by heat-treatment after an optical exposure.
- (3) Since the yield of an acid increases sharply by the acid growth agent, it can reduce the amount of the photo-oxide generating agent used. Consequently, since light can fully permeate to the interior of a sensitization layer, it becomes possible to increase the thickness of a sensitization layer of it sharply.

[Translation done.]

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(54) 【発明の名称】 光反応性組成物、該光反応性組成物を含有した膜反応性高分子組成物及び膜反応性樹脂層

(57) 【要約】

【目的】 本発明は、光反応速度の異なる光反応性組成物を提供することを目的とする。

【構成】 光の作用によって酸を発生する光酸発生剤と、該光酸発生剤より発生した酸により新たに酸を発生する酸増強剤とからなる光反応性組成物である。

【特許請求の範囲】

【請求項1】 光の作用によって酸を発生する光酸発生剤と、該光酸発生剤より発生した酸により新たに酸を発生する酸増強剤とからなる光反応性組成物。

【請求項2】 酸の作用によって分子構造変化を生じる物質を混合した高分子物質、あるいは酸の作用によって分子構造変化を生じる残基を結合した高分子物質中に、光の作用によって酸を発生する光酸発生剤と、該酸の作用によって新たに酸を発生する酸増強剤を存在せしめたことを特徴とする酸反応性高分子組成物。

【請求項3】 酸の作用によって分子構造変化を生じる物質を混合した高分子物質、あるいは酸の作用によって分子構造変化を生じる残基を結合した高分子物質と光酸発生剤とからなる樹脂層に、前記光酸発生剤より発生した酸の作用によって分子構造変化を生じる物質を混合した高分子物質、あるいは酸の作用によって分子構造変化を生じる残基を結合した高分子物質からなる前記の樹脂層とは異なる樹脂層を積層した2層構造を有する酸反応性樹脂層。

【発明の詳細な説明】

【0001】

【産業上の利用分野】 本発明は、光の作用で酸を発生する物質（以下、光酸発生剤と呼ぶ）に、発生した酸によって新たに酸を発生する物質（以下、酸増強剤と呼ぶ）を組み合わせてることにより感光速度を向上させた光反応性組成物に関し、更に、該光反応性組成物を含有した膜反応性高分子組成物及び膜反応性樹脂層に関する。

【0002】

【従来の技術】 従来より光エネルギーを吸収して分子内又は分子間に化学的又は物理的变化を生じる感光性機能を有する材料は種々の方面に利用されている。例えば、光反応によって生じる化学的な構造変化を光学的に検出する画像形成材料として用いたり、モノマーやプレポリマーの光硬化によって表面処理を行う表面被覆処理材料として用いるなど、多方面に利用、実用化されている。しかし、これらの感光性機能を有する材料における感光速度、感光波長領域、解像性は多様であり、目的に応じて適切な特性を有する材料が選択される。

【0003】 感光性機能を有する材料として古くより銀塩感光材料が広く用いられているが、近年、写真製版技術などにおけるように、大量、かつ、高解像性を示す高感度画像形成材料として、高分子材料を主成分とする感光性樹脂が広範囲にわたって用いられるようになった（山岡 亜夫、松永元太郎編、「フोटポリマー・テックノロジー」、日刊工業新聞社（1988年）参照）。高分子系感光性材料は解像性に優れているだけでなく、光反応の選択によって広範囲の感光波長領域が設定できる。また、比較的安価に製造できるなどの多くの利点を有する。しかしながら、感光速度は銀塩感光性材料に比

較するときに比べて低く、最も高感度な高分子系感光性材料とさえども、銀塩材料が示す感光速度の千分の一にも達していないのが現状である。

【0004】 これまでに、高分子系感光性材料の感光速度を向上させるために、さまざまな試みがなされてきた。最も広く開発の对象となってきたのが、光の作用で発生するラジカル種、開始剤として、多数のニルモノマーを連鎖的に重合させる光重合体系である。しかしながら、空気中の酸素と容易に反応するラジカル種が成長種であるために、十分な連鎖反応が進行するとなく終結する。また、ラジカル重合反応の進行とともに急速に形成される高分子ラジカル種内での鎖目構造のために、モノマーの拡散が急速に抑制されて重合が完了することができない。このような原因のために、光重合系の感光速度には本質的な限界値が存在する。

【0005】 一方、光の作用で酸を発生させる、この酸を触媒とするカチオン、含のみならず、さまざまな酸触媒反応を組み合わせてることによって、多様な高分子系感光性材料の創出が可能となった。カチオン重合において、ラジカル重合とは異なり酸による反応の停止効果が無いので高感度が可能であるが、実際には空気中の水分や鎖目構造形成のために、むしろラジカル重合系よりも感光速度は低いのが現状である。また、酸触媒反応を組み込んだ高分子系感光性材料では、光で酸を発生させた後に加熱処理を施して酸触媒反応を誘起させることを原理とする。このため、フोटレジストを主たる利用形態とするこの種の高分子系感光性材料は化学増感型フोटレジストと呼ばれている。しかし、依然として感光速度はラジカル重合系にも及ばないのが現状であり、徹底的な感光速度の向上が求められてきた。

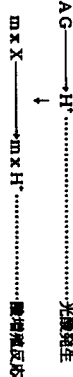
【0006】 更に、光ラジカル重合やカチオン重合を用いたり、あるいは、両者を組み合わせることによって、遊走あるいは酸、引当酸を光源で高感度に硬化する樹脂組成物も広く実用に供せられている。近年、空気中の酸素による阻害効果を受けにくいカチオン重合系は広く開発研究の对象となっており、硬化に際した光酸発生剤や硬化に適用したモノマーやプレポリマーの開環は活発に行われているが、硬化工程の迅速化のために硬化速度の向上が求められている。さらには、光を吸収する原料が分散した樹脂、成物や厚い膜の硬化は表面層のみで起こるために、十分な硬化がもたらされないという本質的な問題点は解かれ、されにまで至っている。また、前述の化学増感型フोटレジストの感光速度が、酸触媒反応を利用しているにもかかわらず、それほど高いものとならない原因として、空気中に浮遊する微量の塩基成分が触媒の放出、用をもちたためと考えられ、或いは、高分子ラジカル種中の酸触媒反応が副反応を引き起こし、このため酸触媒反応が停止することも考えられる。

【0007】

【発明が解決しようとする課題】本発明者は、このような作用で酸を被動的に解決する方法を種々検討した結果、光の作用で酸を発生する物質に、発生した酸によって新たに酸を発生する物質を組み合わせるにより感光速度を著しく向上させた光反応組成物を見出し、本発明を完成したもので、本発明の目的は、光化学反応を増幅させて感光速度を著しく向上させた光反応組成物を提供することである。

【0008】

【課題を解決するための手段】本出願の第1の発明の要旨は、光の作用によって酸を発生する光酸発生剤と、該光酸発生剤より発生した酸により新たに酸を発生する酸増殖剤とからなる光反応性組成物であり、第2の発明の要旨は酸の作用によって分子構造変化を生じる物質を混合した高分子物質、あるいは酸の作用によって分子構造変化を生じる酸基を結合した高分子物質中に、光の作用によって酸を発生する光酸発生剤と、該酸の作用によって新たに酸を発生する酸増殖剤を存在せしめたことを特徴とする酸反応性高分子組成物であり、第3の発明の要旨は酸の作用によって分子構造変化を生じる物質を混合した高分子物質、あるいは酸の作用によって分子構造変化



AG 光酸発生剤； X 酸増殖剤； M 酸分解生成物； N 酸分解生成物

m, n は分子数である。このような酸を増殖する有機化合物を使用して、おおよそ算的に酸を発生させる増殖反応は、該分解反応や増殖反応に類似しているが、有機化学反応としてはこれまでにまったく知られていなかった。酸増殖剤は、熱的にできるだけ安定であるが、酸によって分解し、自ら強酸を発生するもので、比較的強い酸の残基で置換された化合物であり、比較的容易に脱離反応を引き起こして、酸を発生する。したがって、酸触媒反応によつてこの脱離反応を大幅に活性化させることができれば、酸の存在下では安定であるが、酸の存在下では容易に熱化学反応によつて酸を生成させることが可能となる。このような性質を持つ酸増殖剤を光酸発生剤と組み合わせることによつて、飛躍的に感光速度が向上された感光性材料が可能となったのである。

【0009】本発明について詳細に説明する。本発明に

(3)

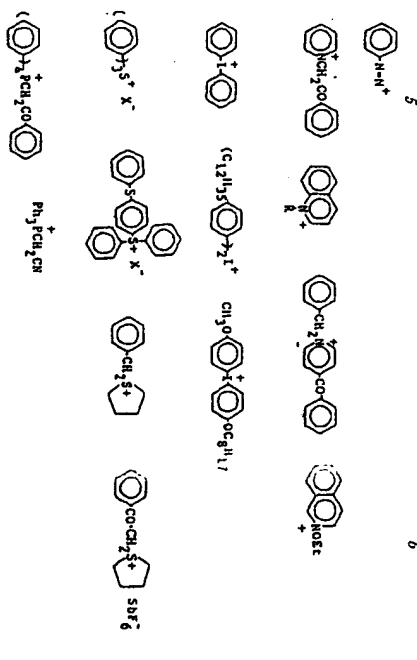
*化を生じる残基を結合した高分子物質と光酸発生剤とからなる樹脂層に、前記光酸発生剤より発生した酸により新たに酸を発生する酸増殖剤と、新たに発生した酸の作用によつて分子構造変化を生じる物質を混合した高分子物質、あるいは酸の作用によつて分子構造変化を生じる残基を結合した高分子物質からなる前記の樹脂層とは異なる樹脂層を積層した2層構造を有する酸反応性樹脂層である。即ち、本発明では酸の作用によつて新たに酸を発生する酸増殖剤を光酸発生剤と組み合わせることによつて、光の作用によつて光酸発生剤より、例えば一つの酸を発生し、該酸が酸増殖剤分子を分解して新たに一つ以上の酸を発生するので、一回の反応で二つ以上の酸分子が増殖して、計2つ以上の酸分子となり、この反応が連鎖的に生じて、酸の発生がおおよそ算的に増えることになる。即ち、このような特性を持つ酸増殖剤を添加により、急激に酸が増し、その結果、塩基性物質による酸触媒反応の停止も防止でき、また、副反応による酸の消失も防止でき、酸触媒反応を大幅に加速することができ、上述の反応原理の原理を图示すると、次のようにな



において光の作用によつて酸を発生する光酸発生剤としては、化学増幅型フォトリソストや光カチオン重合に利用される化合物が用いられる（有機エレクトロニクス材料研究会編、「イメーシング用有機材料」、ぶんしん出版（1993年）、187～192ページ参照）。本発明に好適な化合物の例を以下に挙げる。また、これらの光酸発生剤の感光波長領域を拡大するために、適宜光増殖剤を共存させることもできる。これらの物質の光分解によつて生成する酸は、酸反応性物質とともに酸増殖剤に作用して酸の発生を促進する。以下の光酸発生剤を用いることができる。第1に、ジフエニル、フエニル、ア、ヨードニウム、スルホニウム、ホスホニウムなどの芳香族オニウム化合物のPF₆⁻、AsF₆⁻、SbF₆⁻、CF₃SO₃⁻塩を挙げることができる。オニウム化合物の具体的な例を以下に示す。

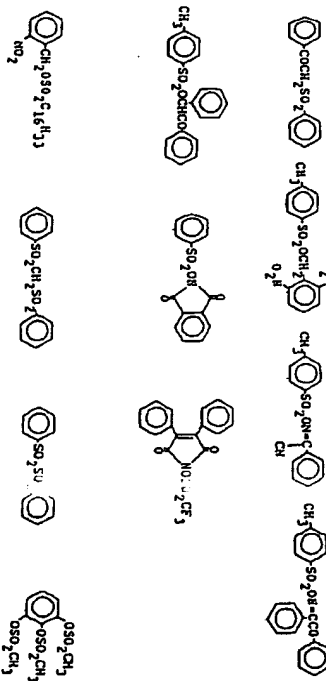
【0010】
【化11】

(4)



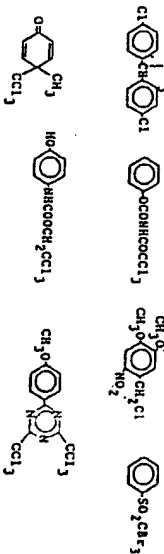
【0011】第2に、スルホニウム酸を発生するスルホニウム化合物を挙げることができる。具体的な化合物を以下に例示する。

* 【0012】
【化2】



【0013】第3に、ハロゲン化水素を光発生するハロゲン化合物も用いることができる。以下に具体的な化合物を例示する。

* 【0014】
【化3】



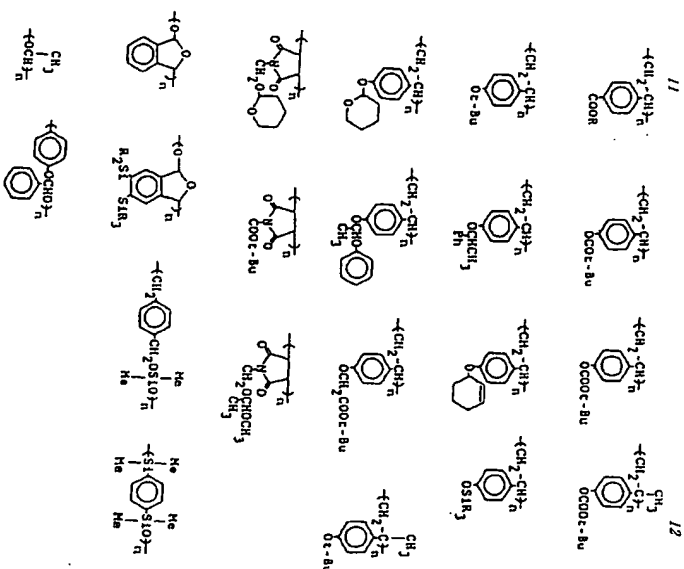
【0015】第4に、酸アレン錯体を挙げることができる。

* 【0016】
【化4】



【0017】本発明で用いられる酸増殖剤は、比較的強

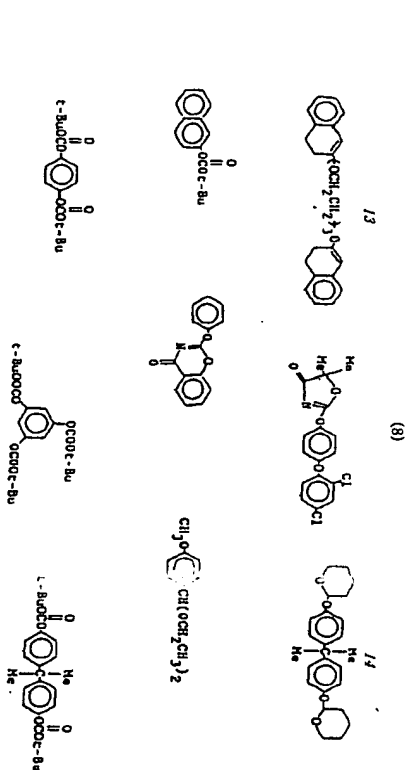
(7)



【0036】第2に、酸反応性低分子化合物を含有する高分子化合物がある。ここでは、酸反応性低分子化合物は樹脂化合物の溶解性を低減する効果を有するものである。溶解抑制剤と呼ばれる。溶解抑制剤として、アセタール化合物、ケタール化合物、カルボキシ酸の第3級エステル、テトラヒドロピラニルエステル、炭酸第3級エステル、トリアルキルシリル基やテトラヒドロピラニル基で保護されたフェノール類、ピナコール誘導体などを挙げることができる。これらの溶解抑制剤を含有する樹脂化合物として、たとえば、ノボラック樹脂、ポリ(p

ーヒドロキシスチレン)、メタクリル酸共重合体、N-メチロール-マレイミド共重合体などをあげることができる。低分子化合物はこれらの樹脂のアルカリ水溶液に対する溶解性を阻害する効果を持つが、酸の作用で分解することによって、この溶解抑制効果が失われて高分子はアルカリ可溶化となる。具体的な溶解抑制剤を以下に例示する。

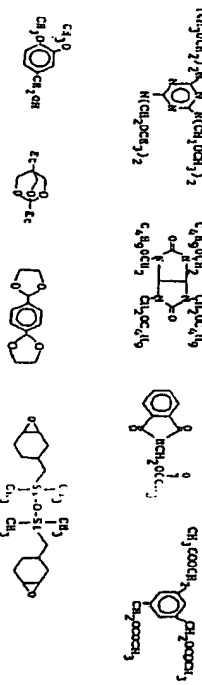
【0037】
【化14】



【0038】第3に、酸触媒反応による縮合反応を高分子の架橋反応に利用する。酸触媒によってカチオンを形成して縮合反応を起こす残基として、ベンジルアルコーン誘導体、メラミン誘導体、N-メタロールイミド誘導体、アセタール誘導体、ピニエーテル誘導体などをあげることができる。また、生成したカチオンと反応する残基としては、フェノール、アルコールなどを挙げるこ

*とができ、これらの残基を有する高分子、たとえば、P-ヒドロキシスチレンの重合体、ノボラック樹脂、ヒドロキシエチルメタクリレートなどの重合体、が好適に用いられる。縮合反応による化合物を以下に例示する。

【0039】
【化15】



【0040】また、この縮合性残基とフェニル残基を合わせた高分子は、それ自体で酸触媒によって架橋を起こすので、本発明に都合がよい。第4に、酸触媒によって重合する残基を持つ高分子が用いられる。カチオン重合性残基として、エポキシ基、オキセタン残基、ピニエーテル基、イソプロペニルフェニル基、環状オルン重合性モノマーあるいはプレポリマーからなる組成物も用いられる。カチオン性モノマー単位として、エポキシ基、オキセタン基、ピニエーテル基、環状オルンモノマーが用いられる。これらのモノマーまたはプレポリマーをピニル系重合体に混和して、自己支持性の凝状物とすることが好ましい。

【0041】について、本発明の感光性樹脂組成物の調整方法を以下に述べる。酸反応性単位を持つ低分子物質を含有する樹脂あるいはそれ自体が酸反応性である高分子化合物に、それに対して0.5～2.0重量%の光線発生剤、および、0.1～2.0重量%の酸増進剤を添加する。上記の光線発生剤の多くは酸とともに、ラジカル種

を発生するので、酸反応性物質とともに、ラジカル重合性モノマーやプレポリマーを混和することもできる。さらには、顔料、染料などを適量添加してもよい。

【0042】均一に分散するために、それぞれを液状に溶解することが好ましい。これらの組成物を凝状にしてから露光して酸として酸の発生させる。について、加熱(ボストベーク)処理を行って酸増進剤の運動的分解を促すとともに、酸触媒反応によって酸反応性物質の構造変化を引き起こす。加熱処理の条件は、露光エネルギー、用いる酸、活性な残基の種類、高分子の種類、などによって変動。したがって、加熱温度は60度から150度の範囲、より好ましくは80度から130度の範囲である。加熱時間は、より好ましくは10分、より好ましくは30秒から5分。この10分加熱時間が短いと酸触媒反応が十分には引き起こされない。この範囲を超える時間では酸増進剤が劇的に引き起こす場合があるし、また、生産性に欠ける。十分な生物質を含む樹脂あるいはそれ自体が酸反応性である樹脂の構造変化に伴う露光と加熱処理前後における、たとえば、溶解性、硬度、膨率、

した。紫外線を露光したのち3分間100℃でポストベークを行ったところ、膜厚の減少は55秒の露光で完結していた。酸増殖剤を無添加の場合には、同じ露光時間では約15%の膜厚の減少にとどまっており、完結するために150秒の露光時間を要した。

【0049】実施例4

実験時に用いたポリマーのジクロロベンゼン溶液に、ホスホリターに対して10重量%のジエタニル（*n*-エタニルネオペンチル）スルホニウム・ヘキサフルオロアンチモネートと参考例5で得たスルホニウムサルーン・ヒドロキシ-2-（*p*-トルエンスルホニルオキシ）-ヘキサンを5重量%加え、ジクロロエタヘン上にスピン塗布して0.5 μ mの薄膜とした。紫外線を露光強度1000で22分間ポストクーアを行った後エタノールで洗浄し、乾燥度を測定した。増粘増利を添加した場合には、10秒の露光時間ですべての膜が溶解したが、無添加では70秒以上露光時間が必要であった。

实施例 5

実施例4において使用したジス-1-メチル-1-ヒ
ロキシ-2-(p-トリエシルホルボキシ)エキサン
のかわりに参考例6で合成した1,2-エポキシ-2-
メチル-3-ヒロキシプロパンを添加した。同様に
して紫外線照射、ボストーク処理、エマルジョン
を行なうところ、乾印厚剤を添加することによってすべて
の膜を溶解するために必要な露光時間を4分の1に短縮
することができた。

【0050】实施例6

メタクリル酸メチルとメタクリル酸2-エチル-2-プロピルエニルとの2:1共重合体 ($M_w = 4,011,014$, $M_w/M_n = 1.74$) に、10重量%のジブニル (P-エニルチオエニル) スルホニウム、ヘキサフルオロアゾベンゼン-2-エチル-2-プロピルエニル-1-ヒドロキシ-2- (P-エニルチオエニル) ホニルオキシ) ヘキサンを5重量%、シリコンエポキシを2重量%、2,3重量%の増粘剤、これに紫外線を照射した後、100°Cで2分間ポストベーク処理を行い、エタノールで現像して複製物を得た。複製時間を4分の1に短縮することができた。

实例 1

実施例Iにおいて使用したジス-1-メチル-1-ヒドロキシ-2-(p-トルエンスルホニルオキシ)-エチル-3-エチル-3-オキシベンゾイル-3-エチル-3-オキシベンゾイルの代わりに参考例7で合成した1-(p-トルエンスルホニルオキシ)-3-エチル-3,3-エチル-3-オキシベンゾイルプロパンを用いて同様な露光、ポストベア、エタノール現像を行った。この乾燥現像を減らすことにより、露光の可溶化を促進するための露光時間を約3分の1に短縮することができた。

【0051】实施例：

実施例 1 で用いたポリマーのシクロヘキサノン溶液に、

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光敏感生剤であるジエニル（*D*-ツェニルチオフェニル）スルホニウム・ヘキサフルオロリンチモネートと1-（*p*-トルエンソルホニルオキシ）-3-エニル-3, 3-エチレンジオキシシクロペンタをそれぞれポリアーミドに封じて10重量%添加して、2枚のポリコン膜で包み上とそれぞれ重畳し布給布して、0.25mmの薄板とした。これらの薄板に直径3mmの円形を通して紫外線照射してから105℃、115℃、125℃で加熱処理を行った。直ちに膜厚の減少に伴う変色が13mmの円形として出現した。その用方は時間とともに増大した。直径が1.2mmになるまでのボイズバック時間は、105℃で7分、115℃で45秒、125℃では30秒であった。これは光で発生した酸が高分子膜内で加熱によつて拡散し、それに伴つて酸濃度の分布による酸発生が次々と引き起こされているためであらう。酸濃度を高くない場合には、このような変化は起こらない。

【0052】実施例9

p-トリチルトルオキシチレンチルホキシベンジエー
 (5, 3.5×10⁴, Mw/Mn=1.69) の2-メ
 トキシエチルアセテートの溶媒に、光硬化剤としての
 2, 3-ジエニル-3-グレート-2-ヒドロ
 キシー-1-(p-トルフェニルホキシエチル) プロパン
 と酸増剤としての1, 5-ニメル-1-(p-トルフェニル)
 ホキシエチル-3-アエニル-3'-エチルベンジ
 オキシプロパンを加えた。この溶液を100℃で30秒ア
 ー1000 rpm で5分塗布し、100℃で30秒ア
 ー1000 rpm で5分時間を要して黄外線を照射して100
 ℃で30秒加熱して現像した。エタノール中に1
 0秒浸漬して現像したところ、高分子膜が完全に可溶化
 する露光時間、酸増剤無添加に比べて約3分の1に
 短縮した。

实例 10

メタクリル酸メチルとメタクリル酸ジメチルとの1:1共重合体の $M_w = 1.5 \times 10^4$, $M_w/M_n = 2.04$ のシロロヘキソリ溶液に、このポリマーに対して3重量%のジエニル (p-エニルチオフェニル) スルホニウム・ヘキサフルオロアンチモネートと3重量%の2-メチル-2-(p-トルエンスルホニル)エチル-3-アクリル酸 α -ピリジンエチルとを加え、さらに、過塩酸化アルミニウム板の上に均しく塗布した。これに乾燥機を時間を要して露光し、3分間100°Cでポストキュアした後、トルエンで板を洗浄し、乾燥機を再び加熱した場合と比較して、共重合体の不溶化に要する露光時間は5分の1に短縮された。

【0053】实施例1

実施例1で用いたポリマーのシクロヘキサン溶液に、
 考例1で得た酸増殖剤である2-メチル-2-(p-
 エンスルホニルオキシ)-3-クトブタン酸tert
 ブチルエステルをこのポリマーに対して10重量% (モ

ノベール単位に対して6キルモル%添加した。この溶液をシリコナーエーラ上にスピン塗布して、27 μ mの厚厚にリソグラフした。比較のために、酸蝕液剤を含まない高分子膜を同様にして調製した。ノボラック樹脂の0.07重量%、ソラノビエラアルコール溶液は、抽出で除去した。5重量%のトリプテニルアルコール、トリブテートを溶解して、これを先に調製した高分子膜上にスピン塗布した。100°Cで1時間ブリークして、光蝕発生剤を含む酸蝕液剤を含む膜の2層からなるシステムは全体として0.62 μ mの厚さとなった。この2層膜に紫外線が露光した後、100°Cでブリーク処理を行い、40°Cのエタノール中で1分現像した。露光時間と現像時間の関係を求めたところ、酸蝕液剤を添加した2層膜は、無添加の2層膜に比べて20%高感度化していることが認められた。

【0054】実施例12

実施例 1 において、光酸発生剤としてトリフェニルスルホニウム・トリフラートの代わりにトリフェニルスルホニウム・ヘキサフルオロアンチモンを添加した 2 層構造の膜について、実施例 10 とまったく同様な露光を行ったところ、酸付置換の添加によって、1.8 倍の高度化が認められた。

实施例 13

実施例 11 で得られたトリフェニルホニウム・ヘキサフルオロアンチモネートを添加した 2 層構造の膜と、公知の化学増幅露光ホトリズトである実施例 1 のポリマーにトリフェニルホニウム・ヘキサフルオロアンチモネートを添加した膜との感度を比較した。その結果、酸増幅剤を分配して含む 2 層構造の膜は化学増幅ホトリズトに対して 2.5 倍の高感度を示した。

10551

【発明の効果】

(1) 感光度が大幅に向上されるので、高感度画面像形成材料に用いることが出来る。
(2) 光阻剤とレジスト処理を組み合わせることによって、光感度樹脂の架橋効率が大幅に向上するので、紫外線硬化型塗料、インク、表面コーティング剤などに効果的に用いることができる。顔料分散した光感度系からなる塗膜は、光感度が表面面積で分散した割合に比例して約十分あるいは内、ではまったく思えないが、本発明によれば、光阻剤への加熱処理によって硬化を完全にすることができる。

(3) 感度の発生は、酸増強剤によって大幅に増大されるから、光感発生剤の使用量を低減することが出来る。その結果、光は感度層内部まで十分に浸透することが出来るから、感光層の厚みを大幅に増大させることが可能となる。

(1) 感光度が大幅に向上されるので、高感度画面像形成材料に用いることが出来る。
(2) 光阻剤とレジスト処理を組み合わせることによって、光感度樹脂の架橋効率が大幅に向上するので、紫外線硬化型塗料、インク、表面コーティング剤などに効果的に用いることができる。顔料分散した光感度系からなる塗膜は、光感度が表面面積で分散した割合に比例して約十分あるいは内、ではまったく思えないが、本発明によれば、光阻剤への加熱処理によって硬化を完全にすることができる。

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